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LETTER TO THE EDITOR

Fermi surface and DHVA effect in $ZrZn_2$ and $TiBe_2$; theory

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Abstract. The bandstructure, density of states, Fermi surface and extremal DHVA areas are presented for $ZrZn_2$ and $TiBe_2$. Arguments are given to suggest the feasibility of DHVA experiments.

Recently the interest in itinerant magnetism in cubic Laves or C15 materials has increased greatly with the prediction (Enz and Matthias 1978, 1979) and discovery (Matthias *et al* 1978) of antiferromagnetism in $TiBe_2$. The isoelectronic isostructural material $ZrZn_2$ is nowadays considered a classic example of a Stoner–Wohlfarth itinerant ferromagnet (de Châtel and Wohlfarth 1973 and references therein).

Primarily because of the difficulty of preparing stoichiometric single crystals, there have been (as far as we know) no direct measurements of the Fermi surface of either of these materials. Such measurements are of primary importance for any detailed understanding of their electronic and magnetic structure. It is our purpose in this letter to present theoretical models in order to stimulate such experiments.

For simplicity we consider both materials in the paramagnetic band limit (weak magnetic effects will change the predicted orbits only slightly).

The bandstructures were calculated using the relativistic APW method as described by Arko and Koelling (1978). The number of points calculated was 125 in 1/48th of the Brillouin zone (89 points on a uniform cubic grid and an additional set of 36 points near high-symmetry lines in order to test degeneracies, splittings etc.). Each of the band levels at 89 points were fitted to a symmetry adapted Fourier series of 44 terms (stars) and had a root mean square fitting error of less than 1 mRyd. The maximum discrete error for the levels near the Fermi level was less than 3 mRyd. (We have found that Fourier fits to relativistic bands show smaller errors than similar fits to non-relativistic bands due to the smaller numbers of crossings along symmetry lines.)

The Fourier series were used to interpolate the bands throughout the Brillouin zone. The density of states was calculated every 1 mRyd by means of a linear gradient method and more than 2000 tetrahedrons were used in 1/48th of the Brillouin zone. The Fermi level was found both from volume compensation and from total electron count. The two values differed by less than 1 mRyd for both materials.

The DHVA orbits were calculated from the Fourier fits. Only orbits centred around the high-symmetry points were considered. The orbital effective masses were calculated as the energy derivatives of the orbit areas with an accuracy of about 1%.

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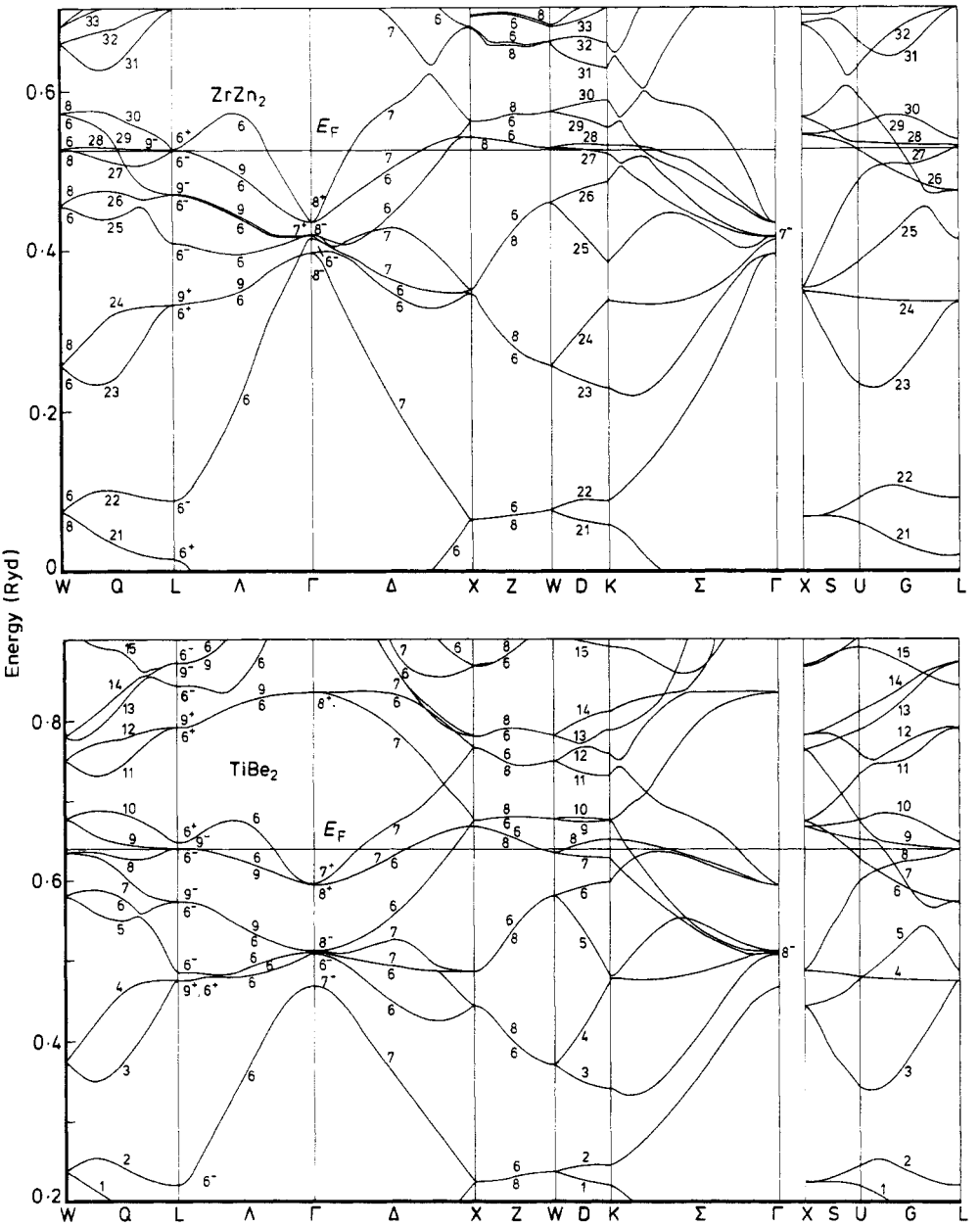

Figure 1. The bandstructure of $ZrZn_2$ and $TiBe_2$ along the high-symmetry lines.

The bandstructures are presented in figure 1. There are 20 Zn d bands below the bottom of the top panel. In the following discussion A and B will refer to the general formula for C15 materials AB_2. The general structure of figure 1 is as follows. Bands 1 and 2 (21 and 22 for $ZrZn_2$) are of mainly B-type s,p character. The character of bands 3 and 4 shows strong dispersion, being of primarily A-type d character at L and also for band 4 at Γ. Elsewhere these bands are of mixed s,p character, centred on the B as well as the A site. The wavefunctions of bands 5 and 6 also have a strong k

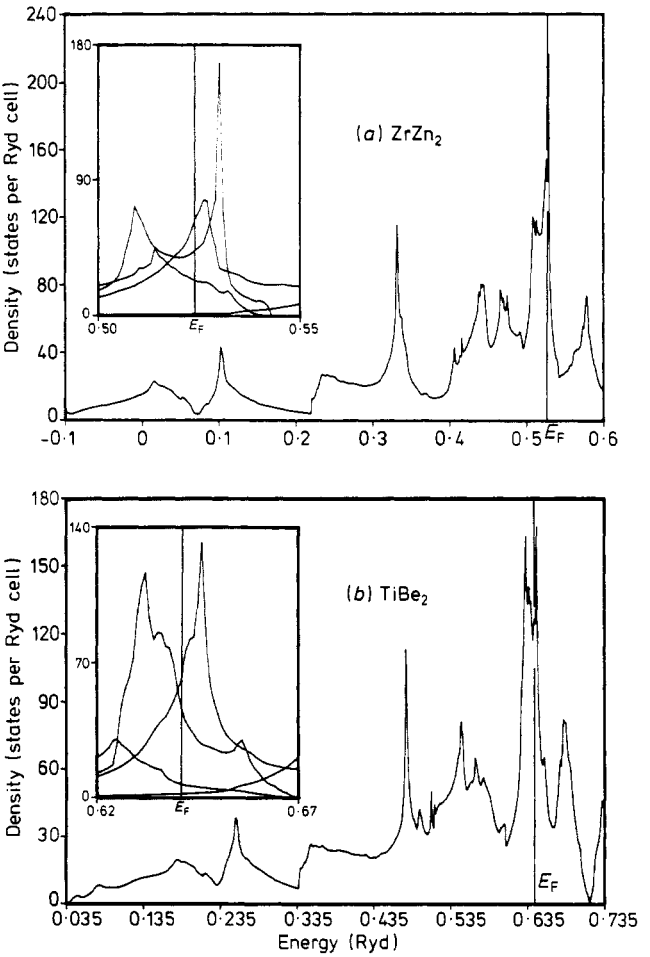

Figure 2. The densities of states of (*a*) $ZrZn_2$ and (*b*) $TiBe_2$. E_F indicates the Fermi level. The insets show separately the contributions to the total density of the four bands intersecting the Fermi level.

dependence. At Γ and W the A-centred d character is the most important. At K and L the bands hybridise strongly, while at X the s,p character is dominant. Bands 7 to 10 (27 to 30 for $ZrZn_2$) are mainly A-centred d bands with various amounts of hybridisation. In general the hybridisation is stronger in $TiBe_2$ than in $ZrZn_2$, consistent with the smaller lattice constant of $TiBe_2$.

The density of states for both materials is given in figure 2, and the insets show the band by band density of states in the immediate vicinity of E_F.

Let us compare this work with the calculation for $ZrZn_2$ by Koelling *et al* (1971). This calculation neglected the scattering by Zn atoms altogether. The lowest bands in this calculation are modified strongly as compared with this calculation, but the states around the Fermi level are nearly unaffected. The density-of-states curves are similar also, except for the more detailed structure more deeply under the Fermi level in the present work. The interactions of the peak states near E_F with the Zn atoms has broadened the peak and reduced its height by a factor of about 1·6.

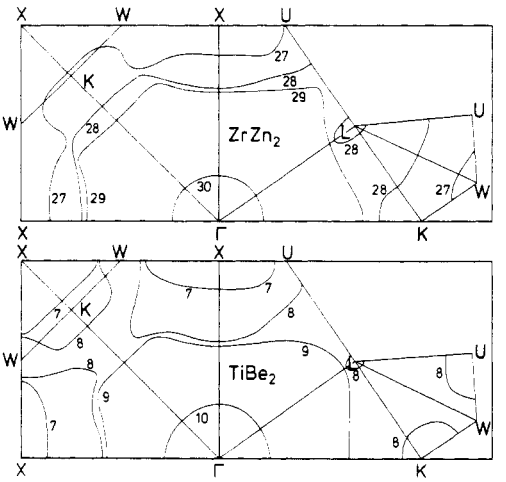

Figure 3. The Fermi surfaces of $ZrZn_2$ and $TiBe_2$.

The intersections of the Fermi surface with the high-symmetry planes is shown in figure 3. The results show two similar electron sheets for bands 29 and 30 of $ZrZn_2$ and the corresponding bands 9 and 10 of $TiBe_2$. Both are closed and centred around Γ. Bands 27 and 28 are found to have different connectivity to bands 7 and 8. Bands 27 and 28 in $ZrZn_2$ form open hole structures similar to the familiar 'junglegyms' of the 5th band sheet of Pd (Mueller *et al* 1970). In $TiBe_2$ the bands 7 and 8 form closed, X centred hole structures.

In figure 4 the angular dependence of the extremal cross sectional areas for the centro-symmetric DHVA orbits is given. The similarities and differences are, of course, a direct consequence of the topologies of figure 3. The broken curves in figure 4(*a*) show the prediction of the X centred 'junglegyms' if they had perfectly cylindrical structures. Finally as a guide for experimental design we have calculated the predicted orbital masses for the high-symmetry directions. They are given in table 1.

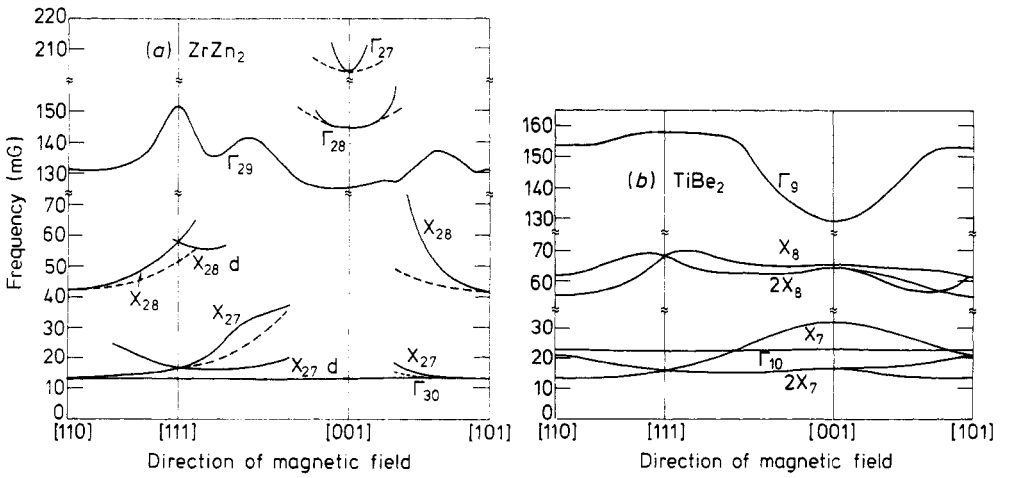

Figure 4. The calculated de Haas–van Alphen spectra for (*a*) $ZrZn_2$ and (*b*) $TiBe_2$. The broken curves for $ZrZn_2$ follow cylindrical surfaces.

Table 1. Theoretical orbital masses for high-symmetry directions.

Magnetic-field direction	Centre of orbit	Band index	Mass	Degeneracy
$ZrZn_2$				
[100]	Γ	27	5·15	1
		28	4·21	1
		29	6·67	1
		30	0·30	1
[111]	X	27	−0·91	3
		28	−2·89	3
	Γ	29	12·56	1
		30	0·30	1
[110]	X	27	−0·61	1
		28	−2·08	1
	Γ	29	6·36	1
		30	0·29	1
$TiBe_2$				
[100]	X	7	−1·22	1
			−0·81	2
		8	−2·50	1
			−3·86	2
	Γ	9	4·39	1
		10	0·46	1
[111]	X	7	−0·61	3
		8	−3·76	3
	Γ	9	6·89	1
		10	0·62	1
[110]	X	7	−0·51	1
			−0·95	2
		8	−1·73	1
			−3·06	2
	Γ	9	8·16	1
		10	0·65	1

A simple model would assume that each orbit has the same many-body enhancement λ as the ratio of the experimentally observed specific heat (428 and 482 states per Ryd cell for $ZrZn_2$ and $TiBe_2$ respectively) and the density of states at the Fermi energy (132 and 118 respectively); see Knapp *et al* (1971) and Stewart *et al* (1979). This leads to an average enhancement of 2·24 for $ZrZn_2$ and 3·08 for $TiBe_2$. The rather high value of the orbital masses of bands 28 and 29, respectively 8 and 9, reflects the peaked character of the density of states and of course, is endemic to the intrinsic interest in these two magnetic materials.

We now consider the possibility of whether the DHVA experiment can actually be carried out in these difficult materials. As is well known $ZrZn_2$ tends to grow off-stoichiometry as $ZrZn_{1\cdot9}$, so that about 5% of the Zn positions are vacant. The overall similarities of the 'no Zn' and the present 'full Zn' band calculations near the Fermi level suggest a smaller scattering effect from such vacancies. We argue further that the spin density map given by Shirane *et al* (1964) qualitatively represents the fractional electronic charge density of the electrons in the immediate vicinity of the Fermi level. The spin density near the Zn atoms is about four times smaller than on the Zr atoms and shows that the magnetic electrons are dominantly confined to the tetrahedral Zr

sublattice. It is difficult to estimate the effective charge of a Zn vacancy. Because of the similarity of the two $ZrZn_2$ band calculations, we believe that such vacancies act as homological impurities.

The effective increase of Dingle temperature per atomic per cent concentration of vacancy will be similar to a homovalent impurity in the light massed neck orbits of the noble metals, i.e., Ag in Au (Springford 1975 and references therein). Hence 20–40 T of magnetic field should be sufficient to see such a 5% 'alloy' or at least the light massed band-30 sheet.

The situation in $TiBe_2$ is better in that crystals appear to grow on-stoichiometry (A L Giorgi 1980, private communication). But the situation is complicated by the antiferromagnetism. Since T_N is only 10 K however, we believe that the application of 20 to 40 T (equivalent to 15–30 K) would either quench the antiferromagnetism completely or drive the system metamagnetic as discussed by Wohlfarth.

Hence we suggest the following: at least one sheet of the complicated Fermi surfaces of these interesting materials will be visible in DHVA experiments. This would test our band models rather sensitively.

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